Effect of Al₂O₃/SiO₂ Ratio on the Viscosity and Structure of Slags

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(Received on July 12, 2011; accepted on December 13, 2011)

The present paper investigates how the mass ratio between Al₂O₃ and SiO₂ (mAl₂O₃/mSiO₂) in slag compositions influences the structure, viscosity and crystallization of the slag melts. The objective is to study the variations in viscosity and structure of slags with increasing mAl₂O₃/mSiO₂ ratio. In practice the results of the study are relevant to the significant changes in slag property caused by the changes in chemical composition during continuous casting of steels containing high amounts of dissolved aluminum.

The viscosity was found to decrease slightly with increasing mAl₂O₃/mSiO₂ ratio up to 0.56. The degree of polymerization for [SiO₄]-tetrahedra was found to decrease with increasing mAl₂O₃/mSiO₂ ratio based on the Fourier Transformation-Infrared Spectra (FT-IR) and Raman spectra, which could explain the observed decrease in viscosity. At mAl₂O₃/mSiO₂ ratios above 0.56, the viscosity was found to abruptly increase which could be caused by the presence of spinel crystals. The activity coefficient was computed and it was found that the activity coefficient of alumina presents negative deviation when mAl₂O₃/mSiO₂ ratio is less than 0.35, while it shows a positive deviation when mAl₂O₃/mSiO₂ ratio exceeds 0.35. This phenomenon may be related to the change of the primary phase region correlating to the phase diagram to the slag composition.

KEY WORDS: viscosity; activity; structure; TRIP steel.

1. Introduction

The quarternary CaO–SiO₂–MgO–Al₂O₃ slag system is very important technologically in a wide range of applications that include ironmaking, steelmaking, ceramics processing, geology and construction industry.¹⁻⁴ The effect of alumina on the structure and physical properties of this slag system has attracted attention during the past decades due to the amphoteric behavior of alumina.⁵⁻⁸ Generally, the researchers studied how varying alumina content influences the structure or physicochemical properties of slag melts through either measurements of viscosity,⁵,⁶ or measurements of structure directly using Fourier transformation infrared spectra (FT-IR),⁷⁻¹⁰ Raman spectra,¹¹,¹² and Neutron diffraction.¹³ Previous studies¹⁴⁻¹⁶ indicated that the substitution of basic oxides (BO) for alumina in ternary BO–SiO₂–Al₂O₃ system at a fixed SiO₂ content enhances the viscosity when the Al₂O₃/BO molar ratio is less than unity, and the viscosity decreases with further increasing Al₂O₃/BO molar ratio. Park et al.⁵,⁶ studied the role of alumina in the quarternary CaO–SiO₂–MgO–Al₂O₃ system at a fixed CaO/ SiO₂ ratio, indicating that the inflection point of alumina transferring from acid oxide to basic oxide is about 10 wt.%. However, the changes in structure and viscosity with varying mAl₂O₃/mSiO₂ ratio have not been investigated so far.

In recent years, Transformation Induced Plasticity (TRIP) steel is becoming relevant with the automotive industry demanding the production of lighter and stiffer car bodies.¹⁷⁻¹⁹ The strengthening effect and required microstructure can be obtained by addition of minor alloying elements such as C, Mn, Al and Si,²⁰⁻²² where Al plays a role to stabilize austenite and to substitute for Si in view of the detrimental effect of Si such as the formed Si-oxides on the surface do not wet with coating alloy resulting in the uncoated regions during galvanizing process.²³,²⁴ The addition of Al in the steel, however, may cause great process control problems due to the chemical reactions between SiO₂ in mold slag and dissolved Al in steel,²⁵,²⁶ which results in a significant increase in the mass ratio between Al₂O₃ and SiO₂ (mAl₂O₃/mSiO₂) ratio in the mold slag as continuous casting progresses. Plant experiments on continuous casting of TRIP steels indicate that a significant change of chemical composition occurred at around 10 to 15 min after the process started and alumina pickup and silica drop seem to pass a critical point.²⁷ In previous studies,²⁸⁻³⁰ the variations of viscosity and crystallization behaviors with increasing mAl₂O₃/mSiO₂ ratio have been investigated, and the experimental results indicated that these thermophysical properties changed with varying mAl₂O₃/mSiO₂ ratio. However, the effect of mAl₂O₃/mSiO₂ ratio on the slag structure has not yet been investigated. The primary purpose of present work is to promote the understanding of the variation of the viscosity and structure with varying mAl₂O₃/mSiO₂ ratio.

2. Experimental

The chemical compositions of the studied slags are shown in Table 1. The present chemical compositions were based on...
a commercial mold slag that is used to cast high Al containing TRIP steel. Fluorine is however a difficult compound to study in a controlled experiment due to its volatile nature. In order to avoid the effect of fluorine on the structure of slag, fluorine was not included in the slag under the present experiment. The chemical compositions were designed considering in the varying mAl2O3/mSiO2 ratio which would result from the chemical reaction between SiO2 in mold slag and dissolved Al in steel. These seven compositions represent a basicity range from 0.11 to 0.82. Slag No.1 is a simplification of a mold slag that is currently under trial in the steel industry for casting of TRIP steels.31) The slags were prepared by mixing reagent grade SiO2, MgO, Al2O3 and CaO oxides. The mixtures were weighted to the designed compositions and mixed in an agate mortar. The mixtures about 200 g was held in a Mo crucible which placed into the reaction chamber of intermediate frequency induction furnace, and then heated to 1 500°C and were held for 1 h to homogenize the slag. These slags were subsequently quenched by pouring the melts onto a copper plate. It should be mentioned that the temperature was monitored by Infrared temperature measurement instrument and the error of measurement is about ±20°C, i.e., the actual temperature might be higher than 1 500°C during the sample preparation. X-ray diffraction revealed that all the quenched samples were amorphous, as shown in Fig. 1 that gives all the XRD results of slags No.1 to No.7. The composition of the samples were analyzed before the experiment by X-Ray Fluorescence spectroscopy (Bruker, S4-Explorer) to confirm the composition, and the results are shown in Table 1. The glassy samples obtained this way were used to carry out the viscosity and structure measurements.

The viscosity measurements were carried out by the rotating cylinder method, with a Brookfield digital viscometer.32) The experimental instrument is shown in Fig. 2, and dimensions of crucible and bob were also included in the figure. This instrument measures the torque of a molybdenum (Mo) spindle rotated at a fixed speed in a Mo crucible filled with the slag melt. The speed scale of spindle is 0–300 rpm. A high temperature furnace system with a maximum temper-
ature limit of 1600°C that monitored by a Pt-10%Rh/Pt thermocouple was used in the instrument. A calibration measurement was carried out at room temperature by using different silicone oil standards with known viscosity of 0.975 Pa·s to 4.85 Pa·s at 298 K. The Mo crucible containing 140 g slag was placed in the even temperature zone of the furnace. In order to avoid the oxidation of Mo crucible and Mo spindle, the purified argon gas was used at a flow rate of 0.3 NL/min. The furnace was heated to 1500°C at a heating rate of 5°C/min and held for 1.5 h to stabilize the temperature and homogenize the slag melt. The Mo spindle was then immersed into the slag melt carefully. Three rotation rates were used for the viscosity measurement of each slag and the time of stabilizing the slag due to rotation rate change was chosen as 120 s. The viscosity data are the average values of the results obtained from three different rotating speeds, and the deviation of the experimental data from the mean value is less than 2% for all the measurements. This also confirms that the slag melt is Newtonian fluid. In order to confirm the reproducibility of viscosity measurements, a repeated experiment for the slag No.4 was carried out. Figure 3 shows the comparative results. It can be seen that the experimental results were matched very well and the deviation is relatively small. Considering the experimental uncertainties usually associated with viscosity measurements, the method of measurements of viscosity was credible.

About 2.0 mg slag powders with 200 mg of KBr were mixed and grinded in an agate mortar, and then was pressed to a 13.0 mm diameter discs for the transmittance infrared spectroscopic measurements. Fourier transform infrared spectroscopy (FTIR) absorption spectra were recorded in the 4000–400 cm−1 range by using Nicolet, Magna-IR 750, equipped with a KBr detector. A spectral resolution of 2 cm−1 was chosen. 20 scans were collected for each slag. The technique employed to obtain the Raman spectra of glassy specimen are laser excitation operating at 532 nm. Its precision of wave number is better than 0.01 cm−1. The experiments were carried out at room temperature and the light source was a semiconductor laser with power of 1 mw.

3. Results and Discussion

Figure 4(a) graphically represents the variation of viscosities of the slags with different m Al2O3/mSiO2 ratio at 1500°C. In order to study the effect of temperature on the viscosity of the slag, the viscosities at 1475°C were also measured and included in the figure. It was found that the viscosity, as expected, increases with decreasing temperature, and decreases gradually with increasing m Al2O3/mSiO2 ratio up to 0.56 for slag No.6, while the viscosity increases dramatically and could not obtain the stable viscosity values for the highest m Al2O3/mSiO2 ratio (0.82) in slag No.7. As Fig. 4(b) shows, the change in viscosity with time for slag No.7 and the observed viscosity increase could be indicative of a pre-
cipitation event, and the variation of viscosity for slag No.5 was also plotted in Fig. 4(c) for a comparison. The change in viscosity with time for slag No.7 may suggest that the slag melt changes from Newtonian fluid to non-Newtonian fluid for slag No.7 due to the occurrence of crystallization. As Fig. 5 shows, the primary crystallization region transforms from the pyroxene to forsterite, and finally spinel (No.7) with increasing m\(\text{Al}_2\text{O}_3/m\text{SiO}_2\) ratio. For slag No.7, the dramatical increase in viscosity could thus be caused by the precipitation of spinel as predicted by Fig. 5. Figure 6 shows the XRD spectra of the quenched slags No.7 and No.1 after the experiments and indeed spinel peaks are detected for slag No.7, while only glassy phase was observed for slag No.1. It can therefore be deduced that the spinel precipitation occurred at the experimental temperature and not during the quenching process of the sample. It should be mentioned that no crystal was found in the premelted slag No.7 during the sample preparation (as Fig. 1 shows). The contradiction may be related to the method used in temperature measurement. The error of infrared temperature measurement instrument is about ±20°C, i.e., the actual temperature was supposed to be over 1500°C. Therefore, no precipitation was detected during the sample preparation. The present study also compared the experimental data with some previous reported results,\textsuperscript{33–35} as Fig. 4(a) shows. It can be noted that the deviation is approximately 20%. Considering the experimental uncertainties among different researchers usually associated with viscosity measurement, the deviation can be acceptable. Furthermore, it can be noted that the degree of viscosity decrease becomes slow at higher m\(\text{Al}_2\text{O}_3/m\text{SiO}_2\) ratio labeled with the line. This variation tendency also can be interpreted by the change of primary phase region correlating to the phase diagram to the slag composition. As Fig. 5 shows, the primary phase changed from pyroxene (\(\text{MgCaSi}_2\text{O}_6\)) phase region to forsterite (\(\text{Mg}_2\text{SiO}_4\)) phase region, and finally spinel phase region (\(\text{MgAl}_2\text{O}_4\)) (Fig. 5), which may result in the change of flow units in the slag melt that can affect the viscosity.\textsuperscript{36} At low m\(\text{Al}_2\text{O}_3/m\text{SiO}_2\) ratio, the affinity between MgO and SiO\(_2\) in the forsterite (or pyroxene) phase region are strong, while the Al\(_2\)O\(_3\) shows the stronger affinity with MgO from SiO\(_2\)–CaO slag melt in spinel phase region as the m\(\text{Al}_2\text{O}_3/m\text{SiO}_2\) ratio is over 0.35. This consequently leads to the results that the degree of viscosity decrease becomes slow in the spinel phase region.

The FT-IR absorption spectra of the slags are presented in Fig. 7. As can be seen, the FT-IR spectrum consists of a strong broad band in the wavenumber range of 1100 to 750 cm\(^{-1}\), a medium intense band between about 630 and 400 cm\(^{-1}\) and a weak band between 750 and 630 cm\(^{-1}\). The bands in the region between 1200 and 750 cm\(^{-1}\) have generally been assigned to symmetric silicon-oxygen stretching vibrations of silicate units containing \([\text{SiO}_4]^{4–}\) tetrahedra.\textsuperscript{11,12} The major bands at 1100–1050 cm\(^{-1}\), 1000–950 cm\(^{-1}\), 900 cm\(^{-1}\) and 850 cm\(^{-1}\) are associated with the presence of bridging oxygen per tetrahedrally coordinated silicon (BO/Si) with three, two, one and zero, respectively (Q\(_3\), Q\(_2\), Q\(_1\), Q\(_0\)), which are labeled in Fig. 7. The appearance of the intense band between about 630 and 400 cm\(^{-1}\) in the silicate glass spectra has been taken as diagnostic of Si–O–Al linkages within the glass structure.\textsuperscript{37} The weak bands observed at 750–630 cm\(^{-1}\) have generally been assigned to symmetric stretching vibrations of \([\text{AlO}_4]^{5–}\) tetrahedral.\textsuperscript{38} It should be mentioned that the band for \([\text{AlO}_6]^{9–}\) octahedra that commonly is found at about 590 cm\(^{-1}\), was not observed under
the present experiment in Fig. 7. In Fig. 7, The band for $[\text{SiO}_4]^{4-}$ tetrahedra which are at about 1100–780 cm$^{-1}$ for slag No.1 shift successively to a lower wavenumber region relating finally at about 1100–737 cm$^{-1}$ for slag No.7. The Raman spectra present the same trend that the shift to lower wavenumber as Fig. 8 shows. The lower wavenumber shift of the Raman spectra with $m_{\text{Al}_2\text{O}_3}/m_{\text{SiO}_2}$ ratio might be caused by two factors. One possible reason is that $[\text{SiO}_4]$ tetrahedra with lower value of (BO/Si) ratio (such as Q1) become more and slag structure has been depolymerized, resulting in a decrease of viscosity. In the present study, the mass ratio between basic oxides (MgO and CaO) and SiO$_2$ increases with increasing $m_{\text{Al}_2\text{O}_3}/m_{\text{SiO}_2}$ ratio. It is a consensus that basic oxides act as network modifier and break the network resulting in the increase of $[\text{SiO}_4]$ tetrahedra with lower value of (BO/Si) ratio. Another possible reason is that the substitution of Si$^4+$ with Al$^{3+}$ results in a shift to lower wavenumber of Raman spectra for $[\text{SiO}_4]$-tetrahedra. In view of the fact that the Al$_2$O$_3$ content increases and SiO$_2$ decreases simultaneously under the present chemical composition and the strength of Al–O bonding is weaker than Si–O bonding, $i.e.$, the decrease in silicate networks with increasing $m_{\text{Al}_2\text{O}_3}/m_{\text{SiO}_2}$ ratio seems to contribute to the decrease in viscosity. Though it is difficult to determine which factor is the main reason, both two aforementioned factors can lower viscosity of slag. The effect of $m_{\text{Al}_2\text{O}_3}/m_{\text{SiO}_2}$ ratio on the relative intensity of FT-IR bands for $[\text{AlO}_4]$-tetrahedra is illustrated in Fig. 9. It can be noted that the relative intensity of $[\text{AlO}_4]$-tetrahedra increases when $m_{\text{Al}_2\text{O}_3}/m_{\text{SiO}_2}$ ratio is less than 0.35 (corresponding slag No.4) and decreases with further increasing alumina content. The relative intensity change of $[\text{AlO}_4]$-tetrahedra may be caused by the change of primary crystalline region from pyroxene (or forsterite) phase region to spinel phase region (Fig. 5), which may result in the change of flow units in the slag melts. As the previous analysis, the Al$^{3+}$ removed from the aluminosilicate due to the combination of Al$_2$O$_3$ and MgO for these slags in spinel phase region, consequently decrease the relative intensity of $[\text{AlO}_4]$-tetrahedra.

**Figure 10** shows the relationship between the $m_{\text{Al}_2\text{O}_3}/m_{\text{SiO}_2}$ ratio and silica and alumina activities of CaO–MgO–Al$_2$O$_3$–SiO$_2$ slags at 1500°C. The activities of silica and alumina were calculated using the ThermoSlag software assuming a pure solid standard state, which is one module of KTH model. In the KTH model, the composition of ionic melts is represented with a Temkin approach. The model database contains the systematically optimized model parameters of the six-component Al$_2$O$_3$–CaO–Fe$_2$O$_3$–MgO–MnO–SiO$_2$, and this enables the model to predict the activities of the oxides in the present slag system. It can be seen that the silica activity decreases while the alumina activity increases with increasing $m_{\text{Al}_2\text{O}_3}/m_{\text{SiO}_2}$ ratio as would be expected. In order to minimize the influence of silica or alumina content on the activity and further understand how the interaction between alumina and silica, the activity coefficients of silica and alumina were calculated as shown in **Fig. 11**. It can be seen that the activity coefficient of alumina increases continuously, while the activity coefficient of silica exhibits a negligible variation with increasing $m_{\text{Al}_2\text{O}_3}/m_{\text{SiO}_2}$ ratio. It should be pointed out that the activity coefficient of alumina shows a negative deviation as the $m_{\text{Al}_2\text{O}_3}/m_{\text{SiO}_2}$ ratio is less than 0.35, while it shows a positive deviation with further increasing $m_{\text{Al}_2\text{O}_3}/m_{\text{SiO}_2}$ ratio. As Fig. 5 shows, the primary crystalline regions changed from pyroxene (MgCaSi$_2$O$_6$), forsterite (Mg$_2$SiO$_4$), and spinel phase region.
Effect of silica and alumina activity coefficients versus mass ratio between $\text{Al}_2\text{O}_3$ and $\text{Si}_2\text{O}_5$ of the $\text{Al}_2\text{O}_3$–$\text{Si}_2\text{O}_5$–MgO–Al₂O₃ slags at 1500°C.

The role of alumina in CaO–SiO₂–MgO–Al₂O₃ slag systems was investigated through measurements of viscosity combined with FT-IR and Raman spectra results. The obtained results are summarized as follows,

(1) The viscosity of slag melts decreases slightly with increasing $\text{mAl}_2\text{O}_3$/m$\text{Si}_2\text{O}_5$ ratio.

(2) The degree of polymerization for $[\text{Si}_2\text{O}_5]$-tetrahedra decreases with increasing $\text{mAl}_2\text{O}_3$/m$\text{Si}_2\text{O}_5$ ratio, resulting in the decrease of viscosity.

(3) The activity coefficient of silica negligibly varies with increasing $\text{mAl}_2\text{O}_3$/m$\text{Si}_2\text{O}_5$ ratio. By contrast, the activity coefficient of alumina increases continuously with increasing $\text{mAl}_2\text{O}_3$/m$\text{Si}_2\text{O}_5$ ratio.

(4) FT-IR and activity coefficient results confirmed the transition point (m$\text{Al}_2\text{O}_3$/m$\text{Si}_2\text{O}_5$$>$0.35), which due to the change of the primary phase region.

(5) The significant change of chemical composition occurred in the real casting of TRIP steel process is due to the change of role of alumina in the slags.

Acknowledgements

The authors wish to express their gratitude to Dr. Q. F. Shu for the thermodynamic calculation. Special thanks are also extended to Dr. L. L. Liu and Mr. S. L. Tang for their help during the viscosity measurements. Financial supports from National Natural Science Foundation of China (50902003, 51172003) and National Key Technology Research and Development Program in 12th Five-year Plan of China (2010BAE00316, 2011BAB02B05) are gratefully acknowledged.

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